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Phase equilibria in the Nb–Ti side of the Nb–Si–Ti system at 1200 °C and its oxidation behavior

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ABSTRACT

Nb–Si based composites are one of the most promising superalloy for the next generation turbine airfoil materials. Alloying Ti can efficiently improve their poor oxidation resistance. In this work, five equilibrium alloys were used to determine the unclear but underlying phase equilibria in the Nb–Ti rich region of the Nb–Si–Ti system at 1200 °C. Convincing evidences on three-phase equilibria of bcc(Nb,Si,Ti) + αNb(Ti)$_5$Si$_3$ + (Nb,Ti)$_3$Si, αNb(Ti)$_5$Si$_3$ + (Nb,Ti)$_3$Si + Ti(Nb)$_5$Si$_3$ and αNb(Ti)$_5$Si$_3$ + (Nb,Ti)$_3$Si + Ti(Nb)$_5$Si$_3$ at 1200 °C were obtained. The important tie-triangle of bcc(Nb,Si,Ti) + αNb(Ti)$_5$Si$_3$ + (Nb,Ti)$_3$Si turns out to be much narrower than the previous calculation. An optimized thermodynamic description validated in the Nb–Ti rich (≤37.5 at.% Si) region between 1000 and 1500 °C of the Nb–Si–Ti system was subsequently acquired based on calculation of phase diagram (Calphad) method. Furthermore, the oxidation kinetics of three equilibrated alloys with increasing Ti content (5–30 at.%) were evaluated at 1050 °C. The one with bcc(Nb,Ti,Si) + (Nb,Ti)$_3$Si equilibrium performed the lowest oxidation rate, which might due to the formation of compact TiO_2 film and the absent of fine eutectic structure bcc(Nb,Si,Ti) + αNb(Ti)$_5$Si$_3$. These knowledge is contributive to understanding the Ti effect on oxidation resistance of Nb–Si based alloys along with the variation of phase constitutions and microstructures.

1. Introduction

In modern gas turbine engines, the airfoil temperature at the hottest location is approaching ~1150 °C, which is close to the limit for nickel-based super alloys [1–3]. With high melting temperature and excellent high temperature strength and creep resistance, Nb–Si based composites, which normally consist of a bcc niobium solid solution with Nb$_3$Si and/or Nb$_5$Si$_3$ intermetallics, are considered as a kind of promising ultra-high temperature structural materials for use in advanced gas turbines and aero-engines up to 1750 °C [4–7]. However, Nb–Si based alloys are subjected to so-called "pest" oxidation at high temperature (≥600 °C), which involved severe crack and spallation of oxidation scales, causing a continuous oxidation process till the failure of alloy [8]. This poor oxidation resistance limits the application of Nb–Si based alloys.

Alloying with Ti is one of the most effective way to improve the oxidation resistance of Nb–Si based alloys [9]. Ti was turned out to react with oxygen before Nb and Si did, forming fine titanium oxide particles in Nb solution and titanium oxide films at phase boundaries, and therefore improve the oxidation resistances of both the silicide and the Nb solid solution [10]. On the other hand, Ti addition plays a key role in controlling the fracture toughness, the strength and the ductility of the bcc niobium solid solution [7,11–15]. However, introducing Ti will also reduce the eutectic temperature (i.e melting point) of the alloy and induce the formation of Ti$_5$Si$_3$ phase, which was found to be detrimental to the creep-rupture strength of the composites [16]. The amount of the Ti addition is suggested to be less than 25 at.% [17].

To better understand and control the effect of Ti addition on the phase constitution, microstructure and subsequent oxidation resistance and mechanical property of the Nb–Si based composites, a thorough understanding on the phase equilibria in Nb–Ti side of the Nb–Si–Ti system at the potential service temperature (≥1150 °C) is essential. A number of investigations have been

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performed in the last two decades [15,17–20].

The isothermal sections near Nb–Ti side at temperatures of 1340 and 1500 °C were experimentally determined by Bewlay et al. [15] through microstructural and micro chemical observations, based on which the isothermals sections at 1150, 1320 and 1350 °C were also estimated. Zhao et al. [17] used diffusion multiples technique to construct three isothermal sections of Nb–Ti–Si at 1000, 1150 and 1200 °C. Near the metal region (<37.5 at.%), the phase equilibrium of $\alpha Nb(Ti)_5Si_3$ + $(Nb,Ti)_3Si$ + $Ti(Nb)_5Si_3$, $Ti(Nb)_5Si_3$ + $(Nb,Ti)_3Si$ + (Nb,Ti,Si) at 1200 °C were determined, and $\alpha Nb(Ti)_5Si_3$ + bcc(Nb,Si,Ti) + $(Nb,Ti)_3Si$ was estimated. The composition range of $(Nb,Ti)_3Si$ was around $Nb_{40}Ti_{35}Si_{25}$ to $Nb_{10}Ti_{65}Si_{25}$ (at. %) at 1200 °C. Xu et al. [18] constructed the isothermal section at 1000 °C in details by using high-efficiency diffusion couple approach, together with 10 button alloys. Their results showed that there were two three-phase equilibria in the Nb–Ti rich region, i.e., bcc(Nb,Si,Ti) + $(Nb,Ti)_3Si$ + $\alpha Nb(Ti)_5Si_3$ and $(Nb,Ti)_3Si$ + $Ti(Nb)_5Si_3$ + $\alpha Nb(Ti)_5Si_3$. However, the solubility of Nb in $(Ti,Nb)_3Si$ was determined to be up to 60 at.% Nb which is quite different from the one (only ~35 at.% Nb) proposed by Zhao et al. [17]. As a result, the estimated three-phase triangle of bcc(Nb,Si,Ti) + $(Nb,Ti)_3Si$ + $\alpha Nb(Ti)_5Si_3$ in Xu's version is much smaller than the other one in Zhao's. Most recently, Zhan et al. [19] investigated the whole composition range of the 500 °C isothermal section for Nb–Si–Ti system, and found that there are eight three-phase equilibria, and that the binary compound Nb_3Si did not exist in this isothermal section.

Despite the above work on phase equilibrium determination, there are still no convincing evidence for two three-phase equilibria, i.e. bcc(Nb,Ti,Si) + $(Nb,Ti)_3Si$ + $\alpha Nb(Ti)_5Si_3$ and $(Nb,Ti)_3Si$ + $Ti(Nb)_5Si_3$ + $\alpha Nb(Ti)_5Si_3$, in the Nb-Ti rich region around 1200 °C [18]. From the aspect of application, these two-phase equilibria are essential for understanding the effect of Ti addition on the phase constitution of Nb–Si based composites, and can help us design proper chemical composition which has appropriate phase fractions of bcc(Nb,Si,Ti), $\alpha Nb(Ti)_5Si_3$ and $(Nb,Ti)_3Si$, and is free of the detrimental phase $Ti(Nb)_5Si_3$.

In the present work, we aim to clarify the unconfirmed three-phase equilibrium relationships, bcc(Nb,Ti,Si) + $(Nb,Ti)_3Si$ + $\alpha Nb(Ti)_5Si_3$ and $(Nb,Ti)_3Si$ + $Ti(Nb)_5Si_3$ + $\alpha Nb(Ti)_5Si_3$, in the near metal region of the Nb–Si–Ti system at 1200 °C, which is one of the most potential service temperature in the advanced aero-engine. Then, based on the experimental isothermal/isopleth sections at 1000–1500 °C and liquidus projections from this work and literature, the Nb–Si–Ti thermodynamic description was optimized based on calculation of phase diagram (Calphad) method. The optimized thermodynamic description validated in the Nb–Ti rich (≤37.5 at.% Si) region between 1000 and 1500 °C of the Nb–Si–Ti system is a very useful guidance for designing Nb–Si based super alloys. Finally, the oxidation kinetics of three equilibrated alloys with Ti content of 5–30 at.% were investigated at 1050 °C, for getting an insight into how Ti effects the oxidation resistance of Nb–Si–Ti alloys along with the variation of phase constitutions and microstructures.

2. Experimental details

Five alloys were prepared and their nominal compositions were listed in Table 1, together with the compositions of 1200 °C-annealed alloys measured by a P400 type inductively coupled plasma emission spectrometer (ICP). The compositions of alloys #1~#5 were selected from the isothermal sections of the Nb–Si–Ti system at 1200 °C calculated with the previous thermodynamic description [21]. The alloys #1, #2 and 3# were used to clarify the tie-triangle of $Ti(Nb)_5Si_3$ + $(Nb,Ti)_3Si$ + (Nb,Ti,Si); alloy #4 was used to clarify the tie-triangle of $\alpha Nb(Ti)_5Si_3$ + $(Nb,Ti)_3Si$ + $Ti(Nb)_5Si_3$; alloy #5 was used to determine the three-phase equilibrium of $(Nb,Ti)_3Si$ + $Ti(Nb)_5Si_3$ + (Nb,Ti,Si).

Table 1
Compositions of Nb–Si–Ti alloys.

No.	Nominal composition (at. %)	ICP composition (at. %)[a]
#1	$Nb_{80.0}Si_{15.0}Ti_{5.0}$	$Nb_{81.3}Si_{13.4}Ti_{5.3}$
#2	$Nb_{72.0}Si_{14.0}Ti_{14.0}$	$Nb_{72.2}Si_{12.3}Ti_{15.5}$
#3	$Nb_{57.5}Si_{12.5}Ti_{30.0}$	$Nb_{57.7}Si_{11.6}Ti_{30.7}$
#4	$Nb_{33.5}Si_{32.6}Ti_{33.9}$	$Nb_{34.6}Si_{30.7}Ti_{34.7}$
#5	$Nb_{9.4}Si_{23.4}Ti_{67.14}$	$Nb_{10.3}Si_{23.3}Ti_{66.3}$

[a] The ICP compositions were obtained from the 1200 °C-annealed alloys.

All alloys were synthesized by a medium frequency induction furnace under high purity argon atmosphere (99.999%) from Nb (99.999%), Ti (99.95%) and Si (99.9%) in a water-cooled copper crucible. Each alloy was re-melted at least five times to ensure their homogeneity. Alloys #1~#5 were cut into small blocks by a wire electro-discharge machine. These small blocks were individually wrapped by tantalum foils and sealed into evacuated quartz capsules. Then annealing at 1200 °C for 720 h was performed in muffle furnaces followed by quenching in ice water. Setting such a long annealing time was to guarantee that the equilibrium (or near equilibrium) state could be obtained.

Standard metallographic procedures were performed for annealed alloys #1~#5, followed by analysis on a EPMA-1720H 4ch type electron probe micro-analyzer (EPMA) and JSM-6700F type scanning electron microcopy (SEM) which is equipped with a Inca X-Max^N energy dispersive spectroscopy (EDS). The standard samples for EPMA measurements were pure Nb (99.99%), Si (99.999%) and Ti (99.9%). The measurement parameters are given in Table S1 in the supplementary information. The relative error for EPMA measurements of Nb, Si and Ti was estimated to be 2–4 wt%, depending on their contents in phases. Meanwhile, the powder samples of the annealed alloys #1~#5 were analyzed by a D/MAX2500 diffractometer with Cu Kα radiation by scanning speed of 4°/min. All the thermodynamic calculations in this work were performed by Pandat software [22].

High temperature (1050 °C) oxidation kinetics was investigated for alloys #1~#3 after being annealed at 1200 °C for 720 h. The samples were grounded into powders with about 70 μm. The mass gain during oxidation was recorded continuously using a WRT-1D thermogravimetry (TG) with accuracy of 0.01 mg. The sample was heating up to 1050 °C in vacuum with the heating rate of 30 °C/min, followed by introducing air into the chamber for oxidation. The oxidation products were analyzed by X-ray diffraction (XRD) on the same diffractometer mentioned previously.

3. Results and discussion

3.1. Phase equilibria in the Nb–Ti rich region at 1200 °C

The backscattered electron (BSE) images and XRD patterns for the annealed alloys are shown in Fig. 1 and Fig. 2, respectively. The identified equilibrium phases at 1200 °C are listed in Table 2, together with their chemical compositions from EPMA measurements. It should be pointed out that the composition of each phase was averaged from three measurements at different positions. Their raw data and standard deviations are given Table S2 in the supplementary information.

Fig. 1 shows the morphologies of the alloys after being annealed at 1200 °C for 720 h. Since all phases are clearly presented and their boundaries can be clearly recognized, we considered that they had already reached equilibrium (or near equilibrium) state. In Fig. 1(a),